CALIFORNIA POLYTECHNIC STATE UNIVERSITY OF SAN LUIS OBISPO

Design and Characterization of a Process for Bulk Synthesis of Cadmium Selenide Quantum Dots

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June 2, 2011

Approval Page

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Date Submitted: June 2, 2011

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Acknowledgements

I would like to thank the following people for their help during my senior project:

- Dr. Richard Savage for guidance and support
- Dr. Philip Costanzo for expertise and insight
- Josh Angell for helping out all the time
- Boeing for project funding
- General LED for project funding

Table of Contents

Table of Figures

List of Tables

Abstract

DESIGN AND CHARACTERIZATION OF A PROCESS FOR BULK SYNTHESIS OF CADMIUM SELENIDE QUANTUM DOTS

By Susan Harada

The objective of the process is to synthesize quantum dots that will fluoresce over the visible spectrum of 450 to 650nm; then to mix the quantum dots together in a polymer matrix so that when illuminated with a blue LED the mixture yields “white” light. The current quantum dot synthesis is a chemical process that involves adding a room temperature Se-TOP precursor to a 225°C Cd precursor solution to cause nucleation and growth of nanoparticles. This method, however, only yields quantum dots that fluoresce in the 520 to 600nm range. In order to create the “white” light phosphor replacement, red quantum dots need to be produced; to resolve this issue, numerous variables were isolated and adjusted. A synthesis temperature of 180°C, 200°C, and 240°C were tested and yielded a variation of growth rates and distribution of sizes, but no change in the fluorescence range. The system appeared to plateau around 600nm despite long reaction times. Cd:Se molar ratios were adjusted and showed that an increase of Se red-shifts the reaction. Various combinations of these variables were tested, but only managed to produce particles fluorescing at 617nm. A long-term test was then run on mixed quantum dot sizes to see if any Ostwald ripening effects would occur, which would be detrimental to the phosphor replacement, but after a month the fluorescence graph indicated no change in the solution. Different ratios of the quantum dot colors were mixed in a cuvette and placed in front of a blue LED, to simulate the application, with a filter and excited by a UV-LED at 90°. Multiple combinations of colors yielded “white” light according to CIE value standards.

Keywords: Quantum Dot, Quantum Confinement, Cadmium Selenide, Colloid Growth, Fluorescence, LED Lighting

1 Introduction and Background

1.0 Current Lighting Technologies

Lights are a large part of our society, with the United States spending approximately 25% of its energy on lighting, which is equivalent to $35 billion a year. Old technologies (e.g. incandescent lighting) are highly inefficient, turning 10% of the energy into light and 90% to heat[1], but are still the most commonly used. This led to the invention of light-emitting diodes (LEDs), which are more energy efficient and longer lasting. To be an acceptable substitute for incandescent and fluorescent lighting though, LEDs need to imitate sunlight by producing a broad spectrum of light. This is currently done by coating a blue LED with a phosphor, but results in a harsh and slightly bluish white light[2] (Figure 1).

Figure 1: (From left to right) Comparison of standard incandescent bulb, "white" LED, and quantum dot lamp[3].

The unnatural white color occurs because phosphors are inefficient at converting energy into light and do not emit evenly across the visible spectrum (large gaps in green and red)[2]. Quantum dots can be a solution due to their tunable wavelength emission and high energy efficiency. A phosphor replacement of various quantum dot colors dispersed in a polymer matrix can emit a more true white light. This should help increase the usage of LEDs and a 2001 Department of Energy study showed that transitioning over to LEDs could save over $115 billion during a 20 year period[4].

1.1 Problem Statement

This experiment is focused on creating a phosphor replacement for consumer white light LEDs, but purchasing commercially-made quantum dots is approximately $45 per milliliter, which is too expensive to use for our experiments. A cheaper synthesis process that produces a full spectrum of quantum dots at Cal Poly San Luis Obispo is needed to achieve this goal.

1.2 Quantum Dot Background

Quantum dots are semiconductor nanocrystals that have been studied since the early 1990's due to their unique optical and electronic properties. These properties all stem from their incredibly small size that ranges from 1 to 10 nm in diameter (Figure 2), which exhibits characteristics between the bulk and molecular level.

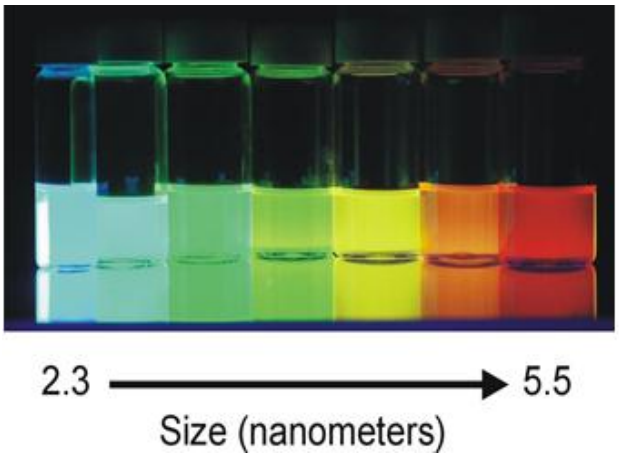

Figure 2: Various particle sizes create different quantum dot colors[5].

1.2.1 Quantum Confinement

Materials are comprised of atoms, which consist of a positively charged nucleus and negatively charged electrons. The electrons are organized in shells (or orbitals) around the nucleus, with increasing energy states as the electron is further away from the nucleus. Each shell can only house a certain number of electrons and the shells cannot overlap (i.e. have the same energy level). The atom always wants to be in the lowest energy state because that is stable; so, electrons will always configure accordingly. As there are more atoms, the number of available shells increases and the electrons will move to occupy

the lowest energy shells. This movement causes orbitals closest to the nucleus to fill and empty orbitals further away. This causes an energy separation and is often referred to as the bandgap, which is fixed for any bulk material. The occupied orbitals are referred to as the valence band and the empty orbitals become the conduction band (Figure 3).

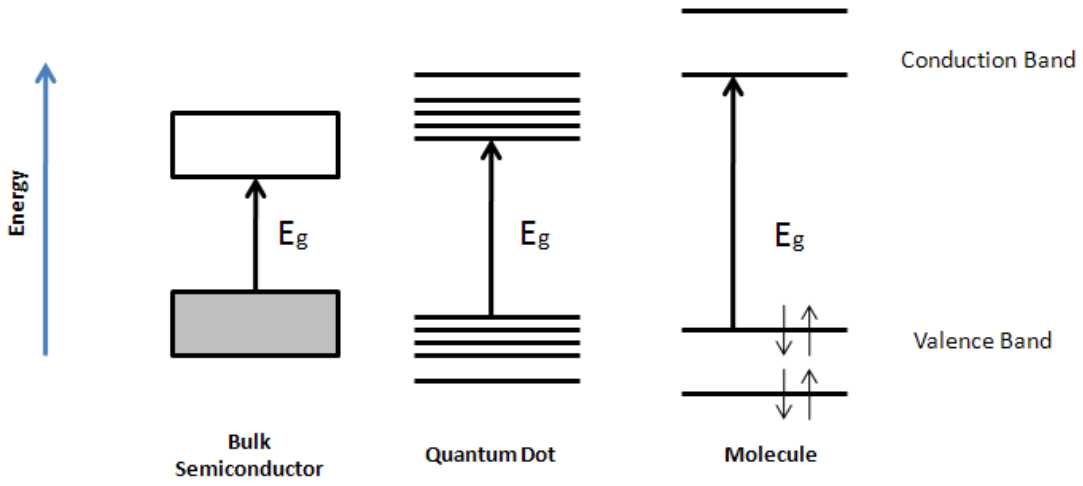

Figure 3: Energy level diagrams where E_g denotes the bandgap.

In bulk materials, there are so many orbitals the bands essentially become continuous. As the number of atoms decreases though, there are larger distances between each shell and form distinct bands.

As noted before, a majority of the electrons will occupy the valence band, but given enough energy (e.g. light) an electron can "jump" the bandgap into the conduction band and leave a "hole" behind. There is a set physical distance that an electron and its "hole" want to be separated, which is called the Exciton Bohr Radius. Quantum confinement is when the physical size of the material is smaller than the Exciton Bohr Radius (Figure 4).

Figure 4: Quantum dots are smaller than the Exciton Bohr Radius, which causes quantum confinement8.

The material then becomes the limiting factor for how far the electron can jump and thus dictate the bandgap of the material[6].

1.2.2 Fluorescence

When an electron is excited into the conduction band, it is unstable due to the large amounts of energy required to sustain its position and almost immediately falls back into the valence band. As the electron falls back down, it releases energy in the form of light (Figure 5).

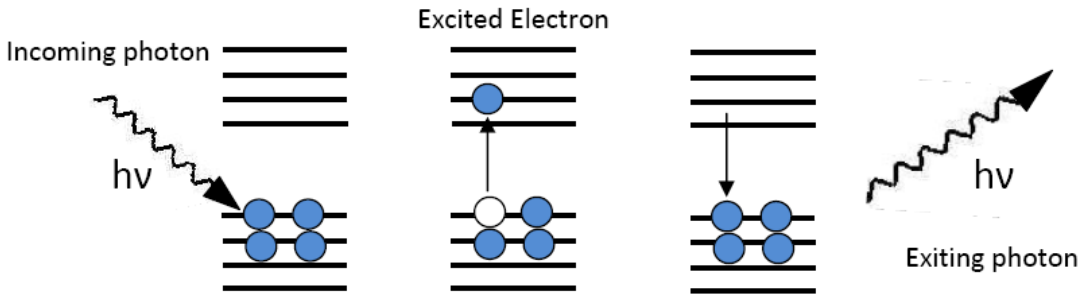

Figure 5: Excited electron falls back into the valence band, releasing light[8].

The energy released is proportional to the bandgap, which in the case of quantum dots, is controlled by the size of the particle. Thus, the size of the quantum dot controls the wavelength emission of the material (Figure 6).

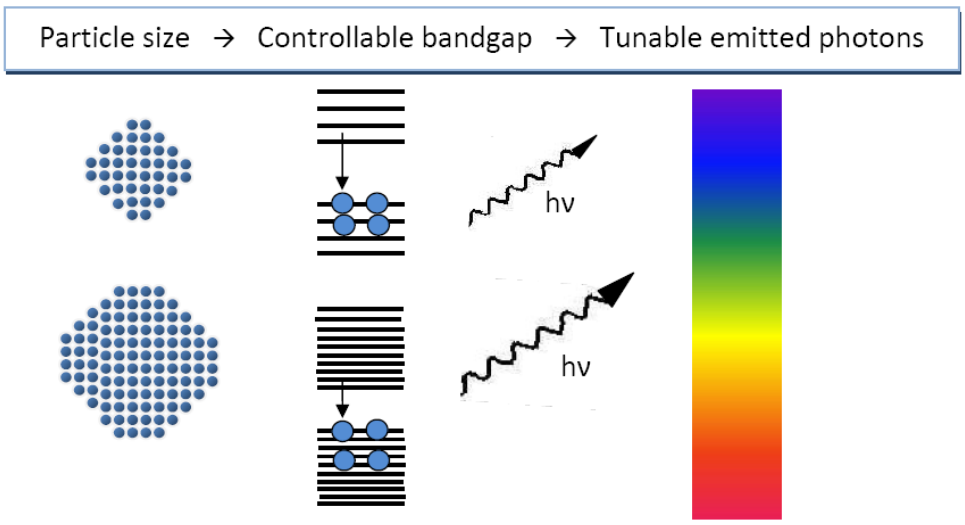

Figure 6: Quantum dot particle size dictates emitted wavelength[8].

As more atoms are added to the nanoparticle to grow, more orbitals are added and shortening the distance between bands. That shorter distance between the shells represents a shorter bandgap (smaller energy separation), which will emit longer wavelengths (towards the red spectrum). The ideal goal is to cover the entire visible spectrum (Table I).

Table I: Wavelengths of the Visible Spectrum

Color	Wavelength
Blue	450nm
Green	500nm
Yellow	550nm
Orange	600nm
Red	650nm

However, green and red are the only necessary colors to theoretically make white light with a blue LED.

1.3 Quantum Dot Synthesis

There are multiple ways to synthesize quantum dots: "top-down", "bottom-up", or a hybrid of both. A "top-down" approach carves out the nanoparticles via lithography or electrochemical processes. "Bottom-up" creates molecular precursors and allows them to react in a solution to produce quantum dots as colloids[6]. A mixture of both techniques is also possible by creating precursors, reacting them as a

gas, and depositing it as a thin film. The “bottom-up” technique was adopted at Cal Poly due to its well-documented ease of production.

1.3.1 Organometallic Colloid Growth

A variety of materials can be used to create quantum dots, but CdSe was selected because it is one of the more well-studied materials. The required materials are easy to procure and the band gap energy (1.7eV or ~720nm) results in emissions within the visible spectrum and into the ultraviolet range. A Se-TOP and Cd precursor are required to start this reaction.

The Se-TOP solution is created first by dissolving selenium powder with trioctylphosphine (TOP) in octadecene, a high-boiling point solvent (Figure 7).

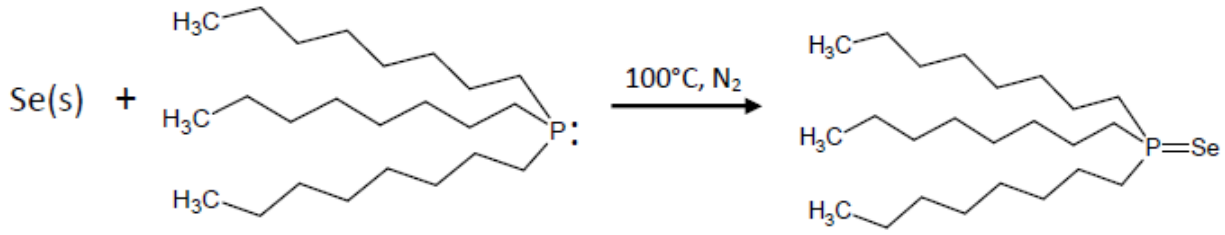

Figure 7: Selenium reacted with trioctylphosphine in an octadecene solvent to create the Se-TOP precursor[8].

The trioctylphosphine is used to help the selenium dissolve and will later coat the quantum dots to promote colloid stability and protect the surface. It is particularly important that this portion of the experiment is run under an inert atmosphere to prevent oxidation of the TOP.

In a separate flask, the Cd precursor is created by dissolving CdO powder in octadecene to isolate the Cd^{+2} ions. Oleic acid is also added to be used, like TOP, as a surfactant on the formed particle. This process must also be run under an inert atmosphere to prevent the released O_2 from potentially oxidizing the TOP when injected.

When these solutions have been made, the Se-TOP solution is added into the Cd precursor at high temperatures to induce nucleation and growth of the nanoparticles (Figure 8).

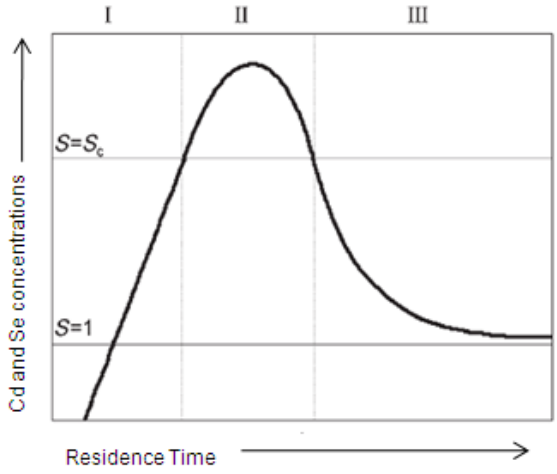

Figure 8: LaMer plot of the nucleation and growth process[7].

Immediately after injection, it is thermodynamically favorable for the Se-TOP bonds to break and have selenium ions in solution. This buildup of Se and Cd ion concentrations is seen on the graph as Stage I, where no reaction has yet occurred. It is not until Stage II where the concentrations have reached a peak that overcome the energy barrier for nucleation and create an explosion of small CdSe particles. The unbonded TOP and oleic acid will then coordinate (bond) to the surfaces of the formed particles to create a coating around the quantum dot. This helps to prevent rapid growth and stabilize the colloid. The myriad of small nanoparticles causes a strong driving force to minimize the enormous surface energy and induces a growth period (Stage III).

1.4 Broader Impacts

Quantum dots are versatile substances that can be used from lighting to bio-imaging applications. This experiment, as mentioned previously, is focused on creating more efficient LEDs which can save billions of dollars in energy consumption. However, quantum dots could also be placed on solar cells to increase efficiency by absorbing a wide range of wavelengths (that would normally go to waste) and emitting a wavelength that can easily be absorbed by the solar cell. Their unique optical properties, like no photo bleaching, are also useful for bio-imaging purposes and could help make breakthroughs in the medical field.

2 Methods and Materials

2.1 Old Process

Quantum dots were first produced at Cal Poly San Luis Obispo in 2009 by Aaron Lichtner, a former student. He developed a cheap, reliable method to synthesize quantum dots with available equipment at Cal Poly, which is still utilized.

2.1.1 Lab Set-Up

A heating mantle and stir plate are used to heat the reaction flask and are placed under a fume hood to reduce exposure to the hazardous vapors and chemicals (Figure 9).

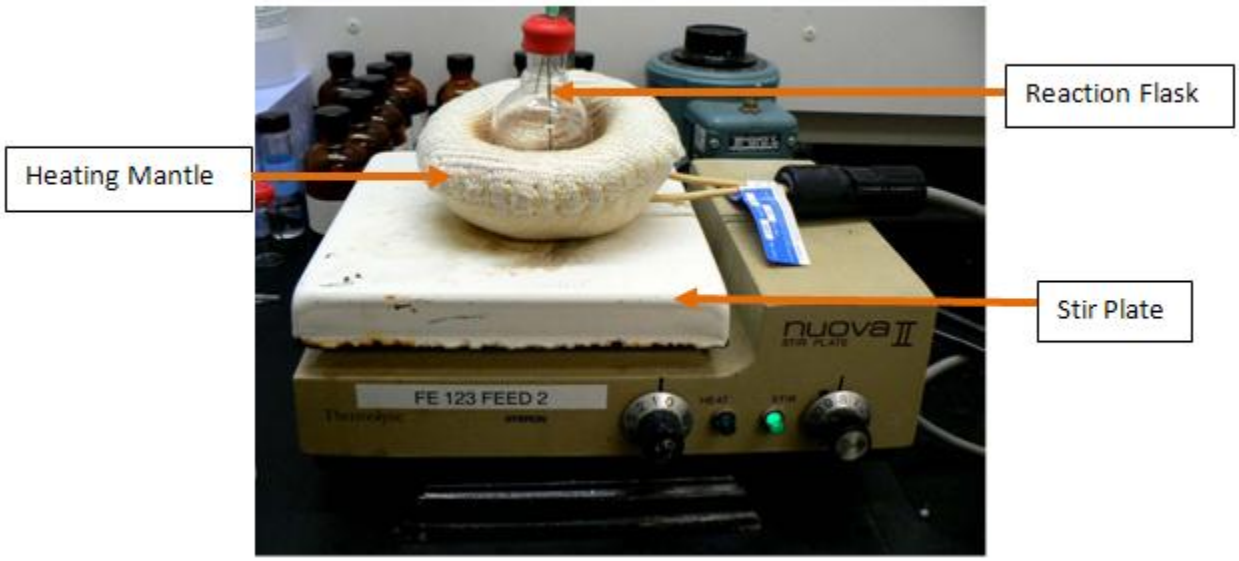

Figure 9: The reaction flask with heating mantle and stir plate is set up under a fume hood.

The stir plate is maintained at a fast rpm to allow the stir bar in the reaction flask to keep the liquid mixture at a uniform temperature.

The synthesis is also run under an inert atmosphere to prevent potential oxidation of the trioctylphosphine (TOP). This is achieved by running low-purity nitrogen gas through a purging system that de-oxygenates all the chemicals and reaction flasks (Figure 10).

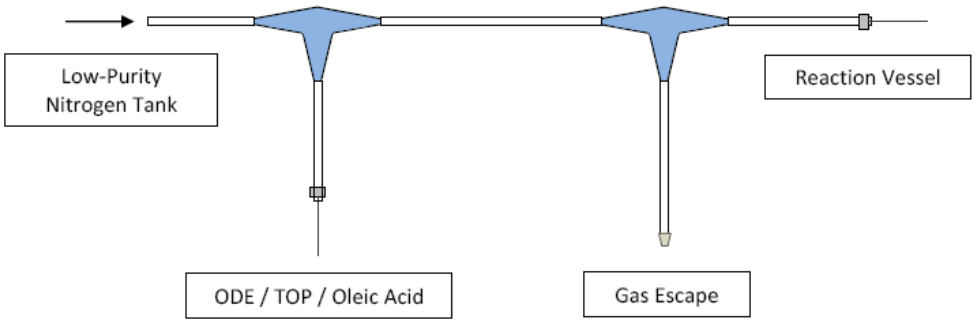

Figure 10: Drawing of the purging system used to de-oxygenate the chemicals and reaction flask[8].

2.1.2 Limitations

The heating mantle, however, proved to have temperature fluctuations after 15 minutes. This resulted in a limitation of reaction times, which restricted the colors produced (Figure 11).

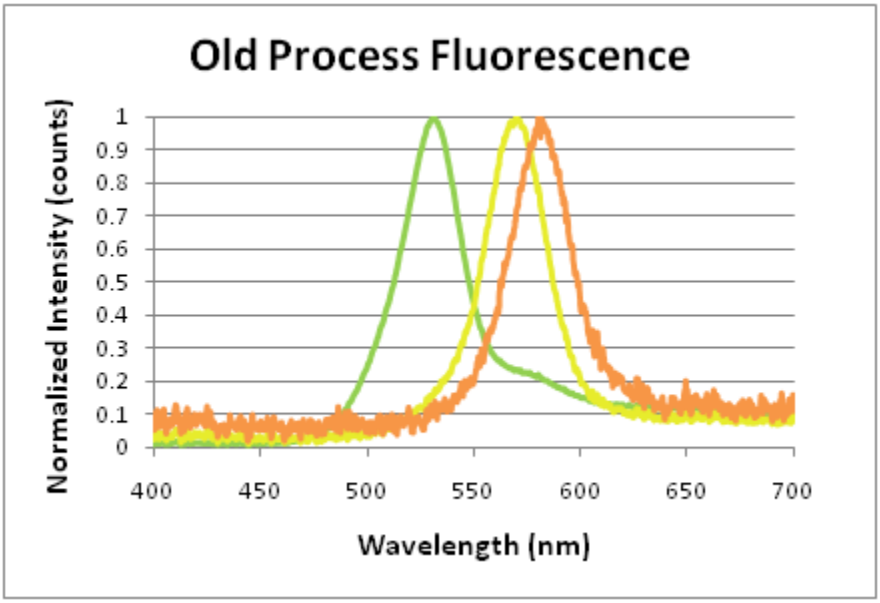

Figure 11: Old process is limited to producing green, yellow, and orange because of the unreliable heating mantle.

The process could only yield green, yellow, and orange. In order to produce white light though, red is also required. To fix this issue, a new heating method needed to be developed for long-term temperature stability.

2.2 New Process

A hot plate with thermocouple and oil bath set-up was purchased to replace the heating mantle (Figure 12).

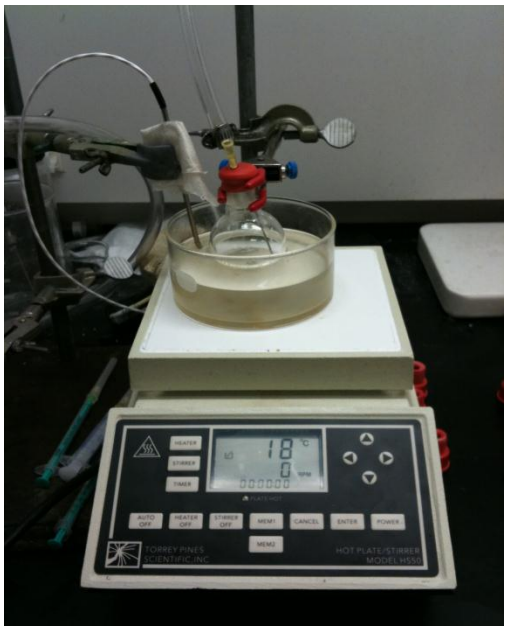

Figure 12: New oil bath set-up with thermocouple feedback for long-term temperature stability.

The thermocouple was placed into the oil bath as a feedback system that allowed the hot plate to maintain a constant temperature. The submersion of the reaction flask in the oil bath (supplemented with the stir bar) also improved temperature uniformity.

2.2.1 Synthesis Procedure

A slightly modified version (to account for the oil bath) of Aaron Lichtner's standard operating procedure, developed by Josh Angell, was used (Appendix A). The chemical synthesis process starts with two precursor solutions that are then mixed together to start the nucleation and growth of the quantum dots. The first precursor made is the Se-TOP solution, which is selenium powder dissolved with trioctylphosphine in a solvent of octadecene (ODE). The second solution is CdO dissolved with oleic acid in a solvent of ODE. Some of the Se-TOP solution is then injected into the Cd precursor at 225°C, which starts the reaction.

The quantity of materials used in a single synthesis produces about 10mL of solution (Table II).

Table II: Materials for a Synthesis

Item	Amount Used	Supplier
CdO	13mg Cadmium Oxide Powder	VWR
Se	30mg Selenium Powder	Sigma-Aldrich
Oleic Acid	0.6mL (tech grade 90%)	Sigma-Aldrich
TOP	0.4mL (tech grade 90%)	Sigma-Aldrich
ODE	11mL (tech grade 90%)	Sigma-Aldrich

2.3 Characterization of Synthesis

Important characteristics of the quantum dot solution are the size distribution and average wavelength emission. A monodisperse particle size is the ideal goal because of the colloid stability and exact emission wavelength. Mixtures of the quantum dots were then analyzed to determine chromaticity values for comparison to a standard white light.

2.3.1 Fluorescence Testing

To examine the quantum dots, samples are placed in UV-transparent quartz cuvettes and excited by an ultraviolet-LED at 90° from the receiving fiber optic to maximize fluorescence readings from the quantum dot emissions and not the light source (Figure 13).

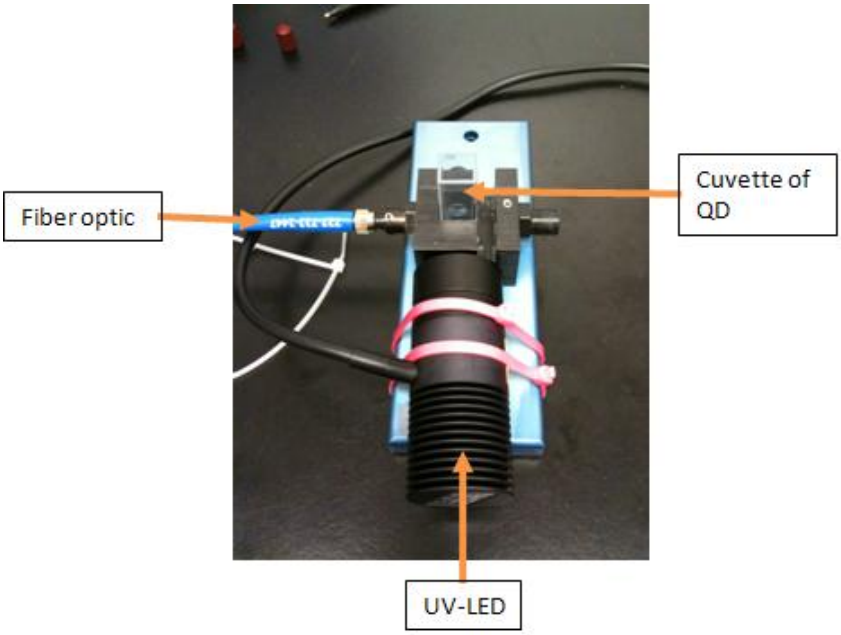

Figure 13: Fluorescence testing set-up for quantum dot characterization.

The fiber optic is connected to a spectrometer, which is connected to and analyzed by Ocean Optics computer software. A black box was also placed over the sample to minimize ambient light distortion to the data. The resulting graphs were then analyzed by finding the central wavelength (CWL) and full-width-half-maximum (FWHM), which is representative of the emission wavelength and size distribution (Figure 14).

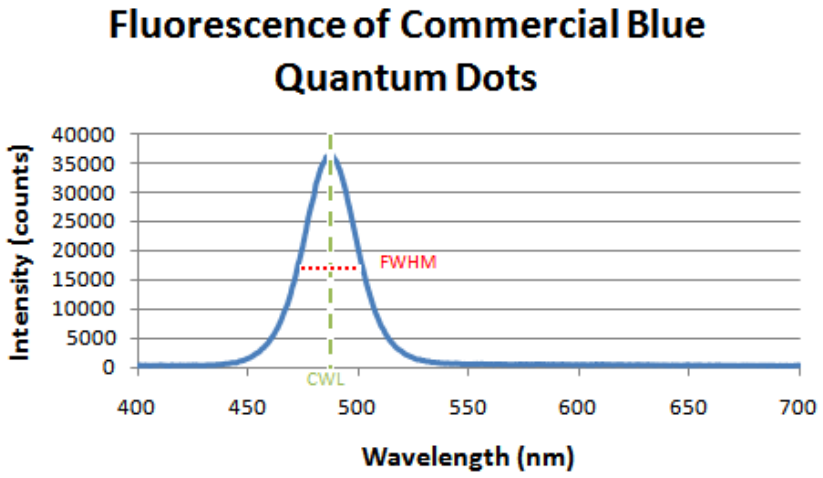

Figure 14: Visual example of calculating the CWL and FWHM of the quantum dot solution.

2.3.2 Ratio Testing

To determine the chromaticity values of the mixture of quantum dot colors, a similar set-up was utilized to mimic the application (Figure 15).

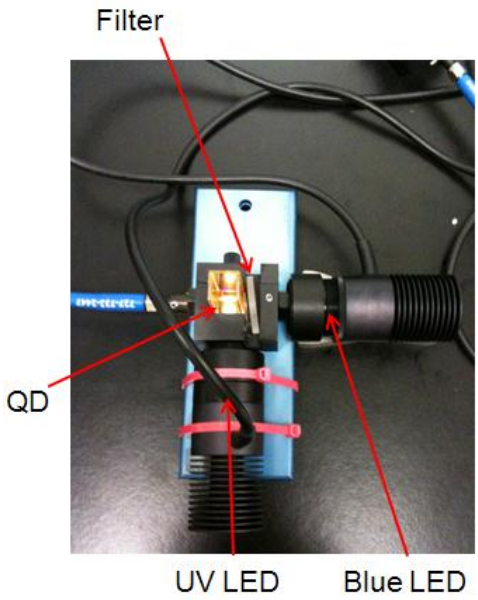

Figure 15: Experimental set-up to mimic the application and retrieve chromaticity values.

The blue LED was placed directly behind the quantum dots, as would be in application; however, the light proved to be dominating in the spectral graph even at the lowest settings. This dominance was cut back by the use of a 2.0 OD optical filter, but was still too intense. An ultraviolet-LED was placed 90° again to increase the fluorescence of the quantum dots, which proved effective. The fiber optic, as before, was connected to a spectrometer and sent through Ocean Optics analysis software (with an integration time of 400ms). The resulting fluorescence data was then used in calculating chromaticity values according to the 1931 CIE standard.

3 Results

3.1 Variable Isolation and Spectrum

In the synthesis process there were many variables that could be altered to achieve the red quantum dots. Each variable was isolated and tested to understand its effect on the reaction.

3.1.1 Time and Temperature

Since the reaction is a nucleation and growth process, temperature and time play a critical role in the resulting nanoparticle size. The standard synthesis of 1mL Se-TOP to the Cd precursor at 225°C was run and extracted samples at various time points (Figure 16).

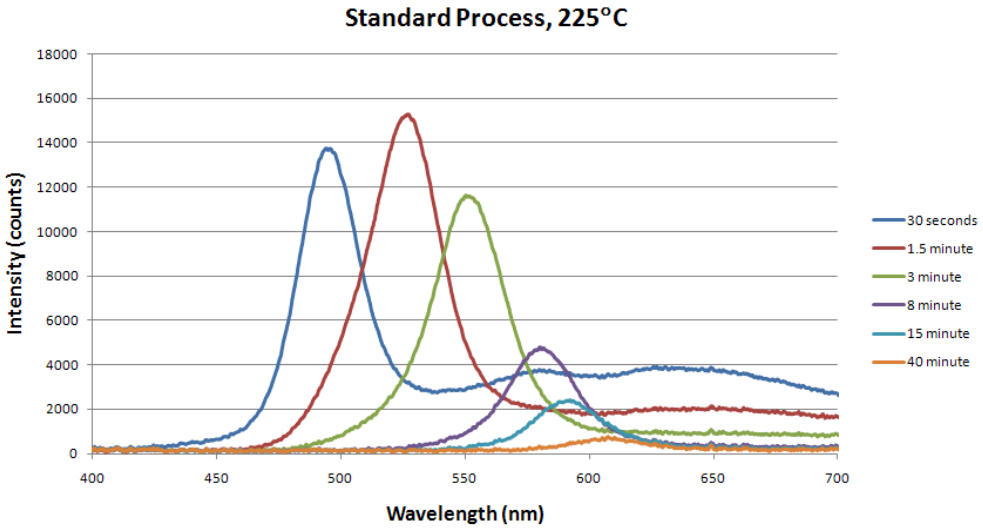

Figure 16: Time effects on standard synthesis at 225°C.

Following nucleation and growth behavior, as time increased the particles grew larger and fluoresced longer wavelengths. Another trend observed was an increase in fluorescence intensity and then a rapid decline.

A standard synthesis of 1mL Se-TOP to Cd precursor was run at various temperatures and extracted samples at 1 minute (Figure 17).

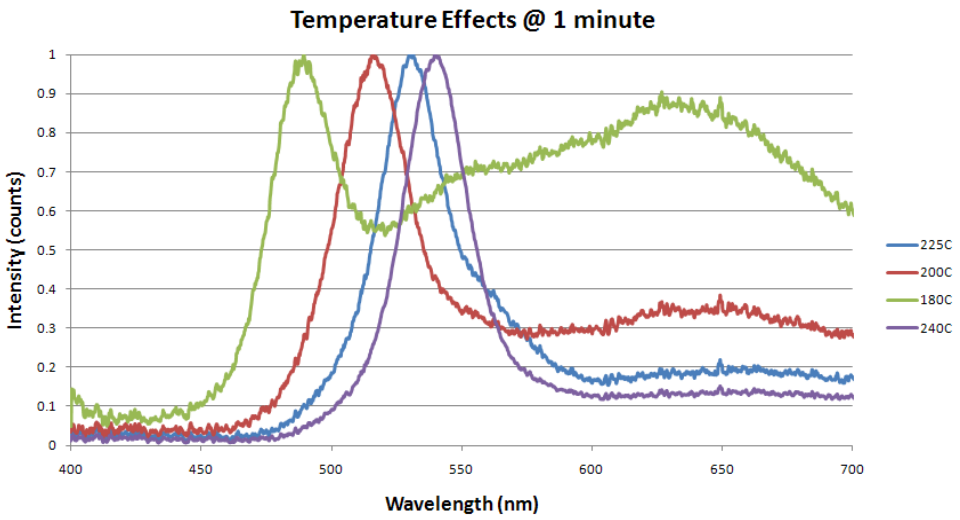

Figure 17: Temperature effects at 1 minute on reaction.

The temperature results also followed nucleation and growth trends with decreased temperature resulting in a decreased growth rate. At the lower temperatures, a significant tail after the fluorescence peak was observed and was indicative of a wide distribution of quantum dot sizes.

3.1.2 Se-TOP Ratio

Literature indicated that increasing the amount selenium into the reaction would cause a red-shift in wavelength emission[9]. This was tested by running reactions at the standard 225°C with various Se-TOP volumes and extracted samples at 1.5 minutes (Figure 18).

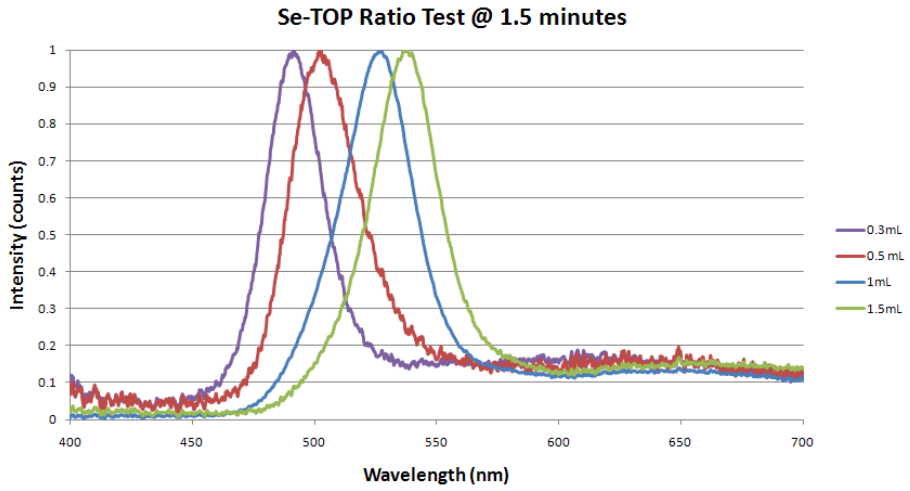

Figure 18: Se-TOP ratio effects at 225°C and extracted at 1.5 minutes.

As was suggested in literature, an increase in Se-TOP shifted the reaction towards red.

3.1.3 Oleic Acid

Oleic acid is used in the reaction as a surfactant to the quantum dot, which helps colloid stability and slow growth rate by acting as a diffusion barrier. Several syntheses were run with the standard procedure (1mL Se-TOP at 225°) with varying amounts of oleic acid in the Cd precursor (Figure 19).

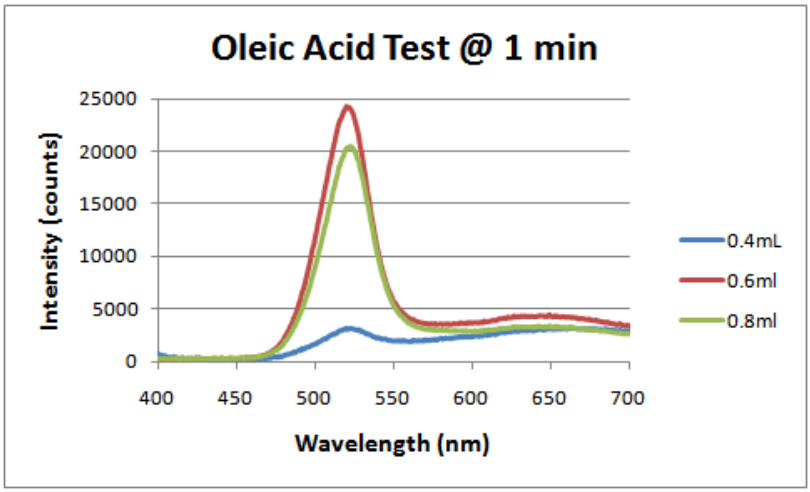

Figure 19: Oleic acid effects at 225°C and extracted at 1 minute.

The results indicated that oleic acid had no effect on the CWL, but at lower concentrations drastically decreased intensity and had a wide distribution of sizes. There was no significant difference in FWHM between the 0.6mL (standard) and 0.8mL, only a slight decrease in fluorescence intensity.

3.1.4 Quenching

The current procedure allows the quantum dots to room cool post-extraction, which could potentially allow the quantum dots to have uneven extended growth. A test was run to compare FWHM values by quenching the samples in an ice bath immediately after extraction (Figure 20).

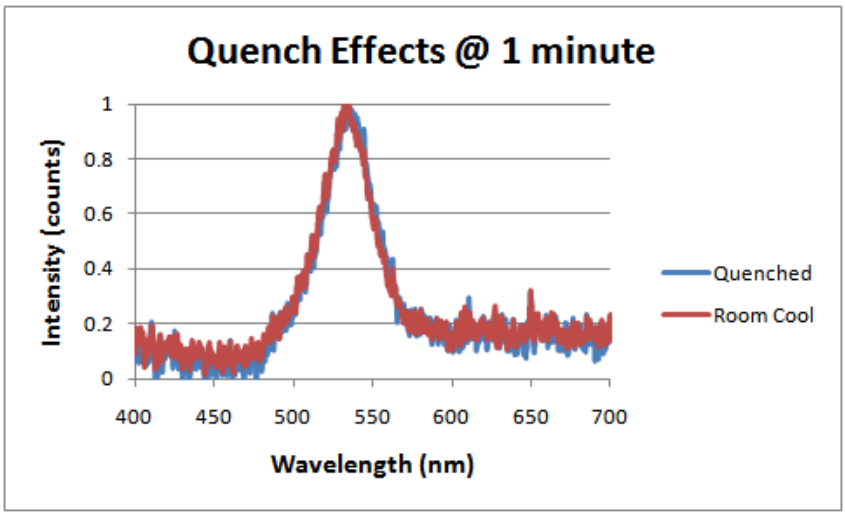

Figure 20: Quench effects on FWHM.

As the graph shows, there appeared to be no benefits to quenching the sample post-extraction.

3.2 Attempts at Achieving Red

With the knowledge of how the various elements affected the synthesis process, multiple factors were varied to try and achieve red quantum dots.

3.2.1 High Temperatures and Long Times

Long-term tests were run at a variety of temperatures ranging from 220°C to 230°C with similar results. The fluorescence tended to peak at around 607nm (Figure 21).

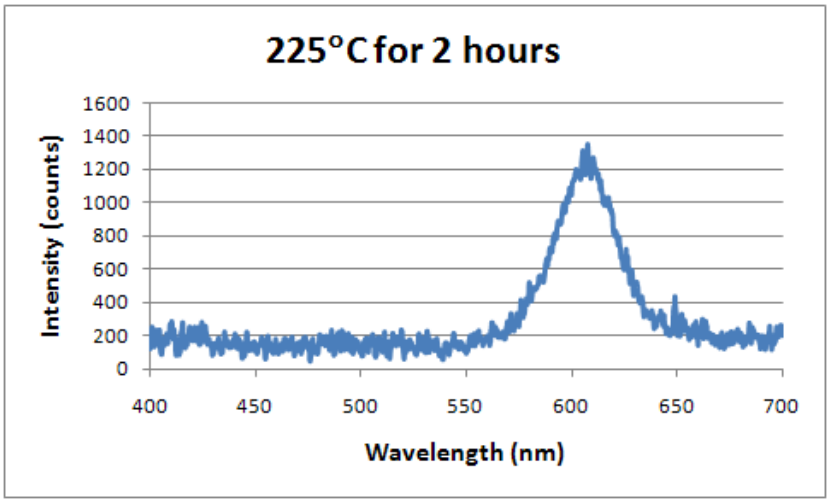

Figure 21: Long times yielded emission peak around 607nm.

3.2.2 Increased Se-TOP and Long Times

The increased Se-TOP was implemented in two ways: injecting more Se-TOP initially and injecting more Se-TOP after the initial reaction. An initial injection of 2mL Se-TOP was run for 55 minutes and yielded quantum dots that poorly fluoresced at 629nm. To increase the fluorescence intensity, the solution was heavily diluted and shifted to an emission of 598nm (Figure 22).

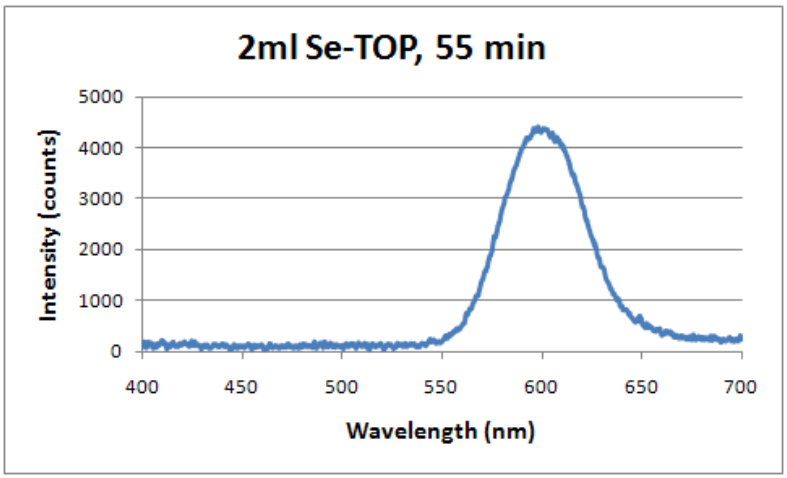

Figure 22: Increased initial Se-TOP and run for 55 minutes.

For the second test, a standard synthesis was run of 1mL Se-TOP, but after an hour an extra 0.5mL Se-TOP was injected into the system. The hour time point was selected because the reaction tends to slow down dramatically around that time. Samples were then extracted at various time points after to observe any extended growth (Figure 23).

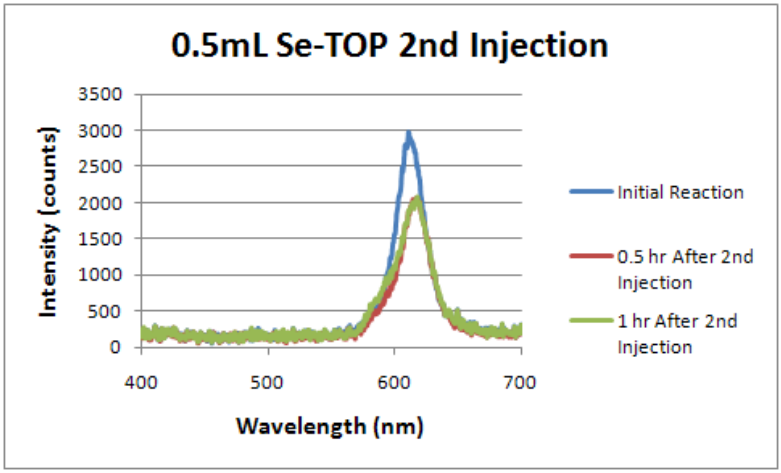

Figure 23: Extra Se-TOP "boost" after initial reaction.

After the second injection, the solution continued to grow and slowed down around an emission of 617nm.

3.3 Testing for White Light

Despite not obtaining red quantum dots, white light should still be achievable. The range and control of tuning the white light, however, will be limited.

3.3.1 Mixed Size Colloid Stability

Prior to trying out various ratios, long-term colloidal stability was checked. Ostwald ripening is a known phenomenon where smaller particles will disassociate and become absorbed by larger particles to decrease surface energy. A mixture of green (small) and orange (larger) quantum dots were mixed and left to equilibrate over a month (Figure 24).

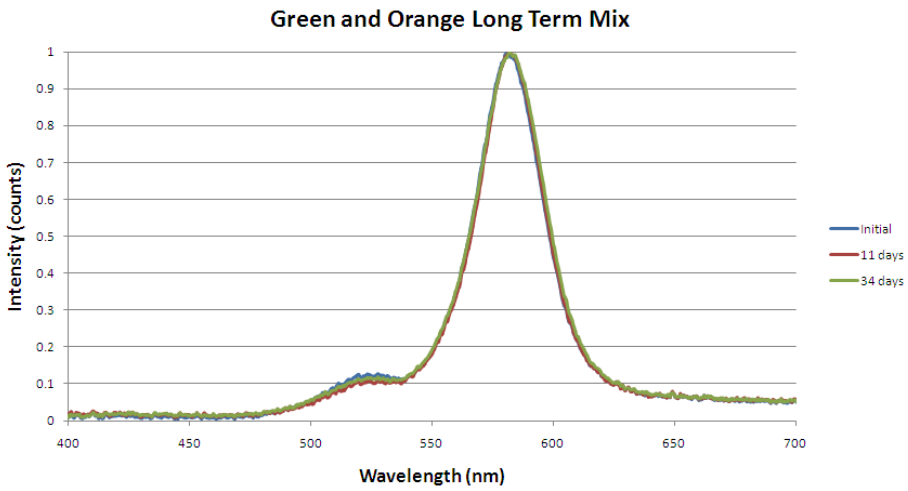

Figure 24: Test of mixed quantum dot sizes for long-term colloidal stability.

Results indicated no Ostwald Ripening effects occurred and stayed the same.

3.3.2 Ratio Tests

Approximately 2mL of solution needed to be put in the cuvette to be fully illuminated by the light source, which was accounted for in the ratios. Large batches of green and dark orange quantum dots were produced for the mixed ratio testing (Table III).

Table III: Emission Wavelength of Mixed Quantum Dots

Color	CWL
Green (uncoated)	533nm
Dark Orange (uncoated)	598nm
Dark Orange (coated)	610nm

Quantum dots are coated to reduce surface defects (that can "trap" electrons), which will increase fluorescence intensity. The ZnS coated dark orange dots used were produced by Josh Angell. A variety of ratios (the full list can be found in Appendix B) yielded CIE values within the white spectrum (Figure 25).

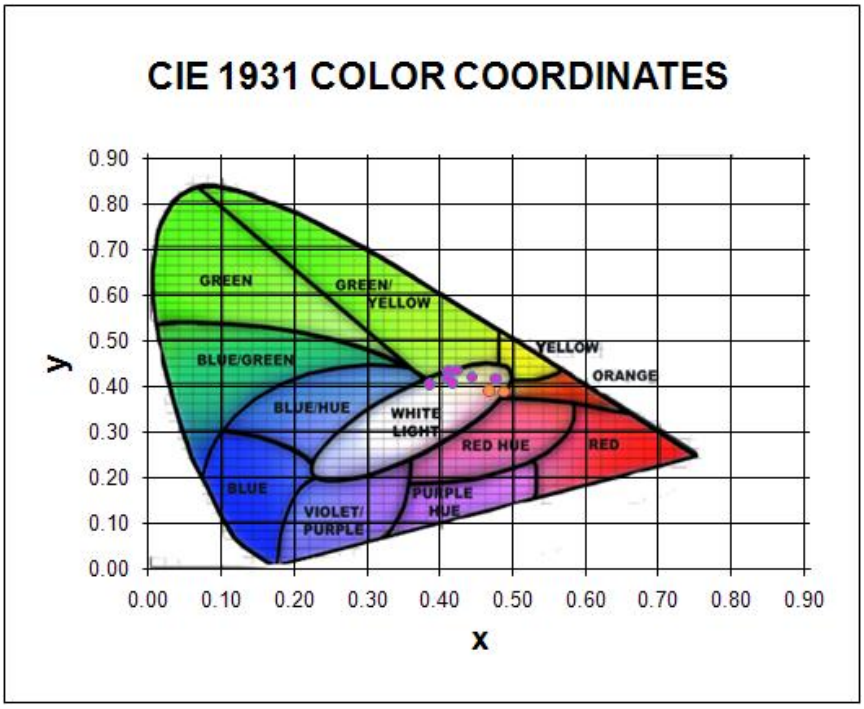

Figure 25: 1931 CIE chromaticity graph of white light ratios.

The purple points used only the synthesized CdSe quantum dots of green and dark orange. The two orange points, however, used the ZnS coated quantum dots for the dark orange.

4 Discussion

4.1 Variable Isolation and Spectrum

4.1.1 Time and Temperature

With increasing time, there was an observed increase and sudden decrease in fluorescence intensity (Figure 16). These fluctuations were caused by the changing sizes of quantum dots and its relation to an optimal concentration. At 30 seconds, there were tons of small particles which may have led to some internal re-absorption of light emission and thus decreased intensity detected at the spectrometer. As the particles grew larger though, those effects went away and approached an optimal concentration around 525nm. The decrease afterwards was caused by the continued growth of the particles and significant decrease in volume concentration; so, there were physically fewer particles fluorescing.

At lower temperatures there was an increase in size distributions with decreased growth rate (Figure 17). The growth rates varied due to thermal energy of the system, with the more energy available the faster the reaction could occur. Along the same lines, the lower temperatures (lower thermal energy) caused multiple nucleation and growth stages to occur, which led to the formation of a wide variety of sizes. As the temperature increased (more thermal energy), the nucleation and growth stages could be separated into single events: burst of nucleation and growth of all the particles.

4.1.2 Se-TOP Ratios

As the LaMer nucleation and growth plot depicted, there is a certain concentration of ions needed to begin the nucleation process (Figure 8). Increasing the amount of Se-TOP increased the amount of Se ions, which allowed the reaction to surpass the energy barrier faster to begin the nucleation stage sooner.

4.1.3 Oleic Acid

Decreasing the oleic acid volumes in the Cd precursor caused a significant decline in fluorescence intensity and had a wide distribution of sizes (Figure 19). At 0.4mL of oleic acid, there were not enough molecules to fully coat all the quantum dots which caused open areas on the surface for conglomeration. Thus many quantum dots grew to be larger than the Exciton Bohr Radius and lost the quantum confinement effects.

Increasing the oleic acid concentrations proved to have no effect on CWL or FWHM, but had decreased fluorescence. This might be due to an excess of molecules in the solvent, which may have caused light scattering and decreased the amount of excitation of the quantum dots.

4.1.4 Quenching

Quenching the samples had no effects on the FWHM of the samples (Figure 20). The initial extraction of the solution into the glass syringe must be a large enough decrease in temperature to arrest the reaction.

4.2 Inability to get Red

With the new oil bath set-up, temperature stability was no longer the limitation on achieving red quantum dots. The new issue appeared to be the extremely low concentrations of quantum dots as the particles became large. Either more concentrated batches need to be run or multiple syntheses need to be combined and concentrated to produce the necessary fluorescence intensity.

4.3 Cost Analysis

A list of chemicals and equipment was compiled (Appendix C) and showed the average cost of one synthesis (about 10mL) is about $9.17.

5 Conclusions

Temperature and time, as expected, held the most control over the resulting quantum dot sizes. Se-TOP ratios also proved to have an effect on growth rates though. Despite still not producing red quantum dots, various ratios of green and dark orange were able to achieve white light by 1931 CIE standards. The mixture was also proved to be stable for over a month. The synthesis process also produced quantum dots at around $0.92 per milliliter, as opposed to the $45 per milliliter for commercial dots.

6 Future Work

Further process optimization should be looked into to try and achieve red quantum dots. Testing new solvents such as trioctylphosphine oxide (TOPO) or heat transfer fluid (e.g. Dowtherm A) could aid in better synthesis control[10].

Size-selecting quantum dots through precipitation methods and filtering out the excess molecules in solvent could help in light emission control and provide fine-tuning abilities on the white light output.

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Appendix A

CdSe Quantum Dot Synthesis Reaction and Characterization Procedures
The first part of this procedure outlines 3 different techniques (Purging, Syringing, & Oil Bath Operation) which are required for quantum dot synthesis. The second part contains instructions to create the selenium/cadmium precursors and then react them to synthesize CdSe quantum dots.

Chemicals

- 13 mg Cadmium Oxide Powder
- 33 mg Selenium Powder
- 0.6 mL Oleic Acid (tech grade 90%)
- 15 mL Octadecene (tech grade 90%)
- 0.4 mL Trioctylphosphine (tech grade 90%)
- Toluene and Acetone for cleanup

Equipment

- 2 – 50mL 14/20 1-neck or 3-neck Round Bottom Flasks
- 2 – 1mL Disposable Plastic Syringes
- 2 – 3mL Disposable Plastic Syringes
- 1 – 5cc Glass Syringe, Luer Lock Tip
- 1 – Veterinary Tip, 18 gauge, 3” SS Needle
- 2 – Small Stir Bars
- 3 to 5 – 7.5 mL Borosilicate Vials
- 1 – Medium-Sized Beaker (150 mL)
- 2 to 4 – Rubber Septa
- Hot/Stir Plate with RTD Probe
- Crystallization Dish
- ~ 200 mL – High Temperature Silicone Oil
- Chemical Spatula
- Kimwipes
- Thermocouple
- Analytical Balance
- Stopwatch
- Latex or Nitrile Gloves

Chemical Disposal
All chemicals and equipment used during the quantum dot synthesis must be properly disposed of. Currently there is a vessel for liquid waste and a container for solid wastes such as needles, syringes, kimwipes, etc. which are stored in the yellow, hazardous chemical cabinet in the nanotech lab (Bldg. 41-205).

Preparing Chemical Bottles

1. Fill a clean dry bottle with the desired chemical.

2. Fit a rubber septum into the top of the bottle.

3. Either purge the solution if it is to be used immediately or store it for later use.

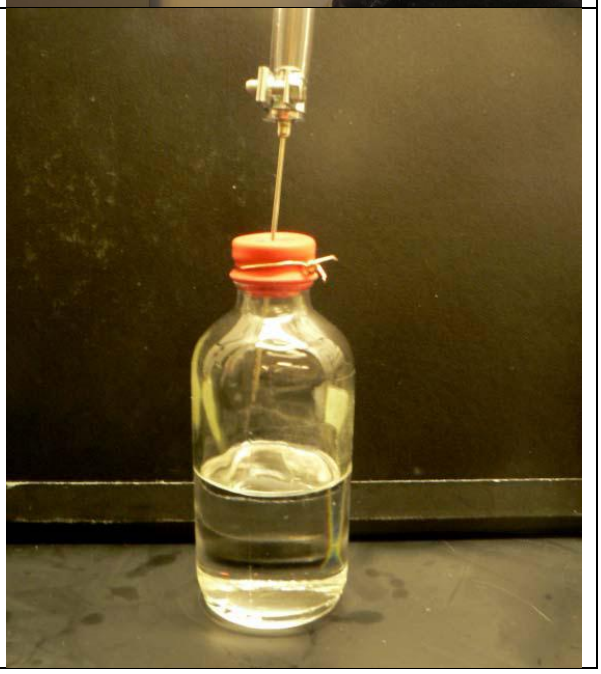
Purging Procedure

This procedure is to be used for any chemical and/or reaction vessel needing purging.

1. Fill a large beaker with water until it is ¾ full.
2. Lower N_2 tank gas escape hose into beaker.

3. Fully open valve on top of tank.
4. Fully open left knob on valve.
5. Open middle knob on valve (“increase”) until bubbles start to appear in the beaker. Maintain this gas flow throughout the procedure.

6. Insert N_2 purge needle into center of septum. Make sure the needle is above the level of the liquid.

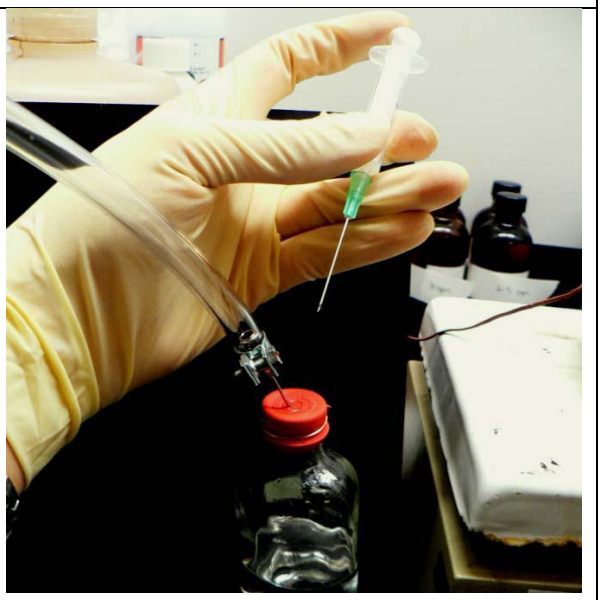


7. Insert a vent needle into the septum next to the N_2 purge needle. Make sure it is above the level of the liquid.	
8. After inserting the vent needle, lower the purge needle so that the tip is submerged in the liquid. Bubbles should begin to form in the liquid. If the needle cannot be submerged below the level of the liquid, either more chemical can be added or the bottle can be carefully tilted. 9. Allow to bubble for at least 10 minutes to remove oxygen from the chemical.	

Syringing Procedure

This procedure is a method of transferring a chemical from one purged vessel into another without the introduction of oxygen. All solutions must be properly purged with N_2 before using this procedure.

1. Remove a disposable plastic syringe from its packaging.	
2. Pull the N_2 purge needle up so that it is above the level of the liquid. No bubbles should be forming at this point.	

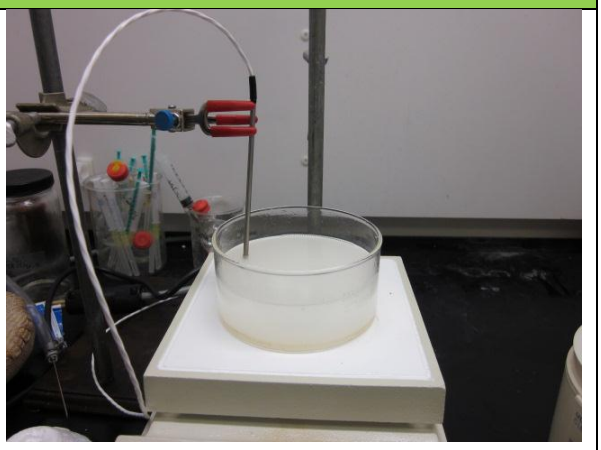
3. Insert the tip of the syringe into the venting needle. 4. Draw N_2 gas up into the syringe.	
5. Remove the N_2 filled needle and syringe from the septum and fully expel all the N_2 gas by plunging the syringe down. Make sure to expel the syringe away from yourself in the hood. 6. Reinsert the needle and syringe into the septum. 7. Repeat the filling and expelling process twice more. This removes any oxygen in the syringe. 8. Reinsert the needle and syringe then pull up the syringe to once again fill the syringe with N_2. Do not remove the syringe from the flask.	

9. Fully pull out the N_2 purge needle.	
10. Plunge down the N_2 filled syringe to create positive pressure in the vessel.	

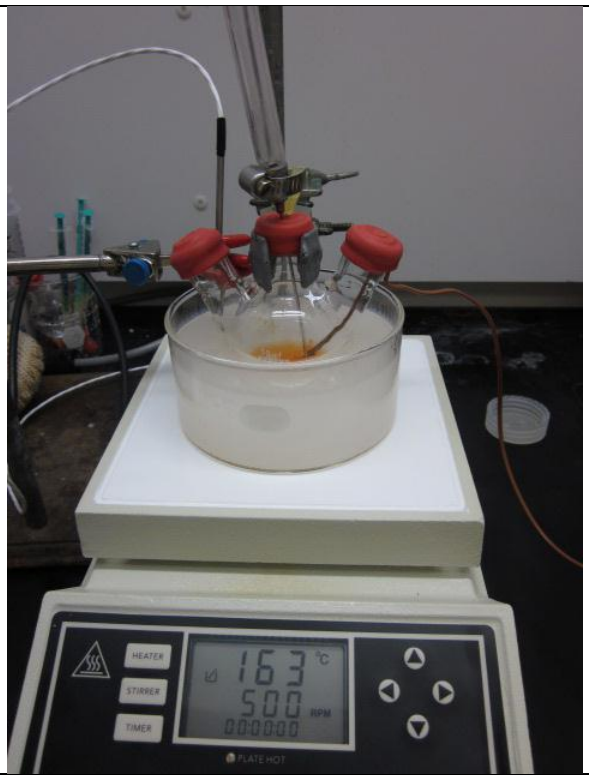
11. Invert the chemical vessel and syringe. 12. Slowly draw out the desired amount of solution into the syringe. Make sure to keep the needle tip in the liquid to prevent gas from entering the syringe.	
13. Quickly and carefully insert the needle into the center of the septum of the desired vessel and slowly plunge down until all the liquid is expelled. 14. If more of the purged chemical is needed, quickly reinsert the syringe into the purged solution and draw out more chemical. 15. Chemicals must be repurged if left for longer than 10 minutes.	

Oil Bath Operation

1. Fill crystallization dish with ~200 mL high temperature silicone oil.
2. Place dish on hot plate.
3. Put paper clip into dish, which will act as a stir rod for the oil.
4. Clamp RTD probe in clamp on ring stand so that it is in the oil bath without touching the glass.

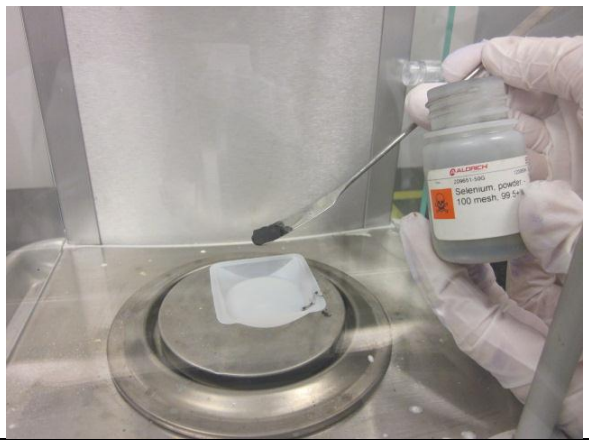


5. Press heater button on plate.
   Set to desired temperature.
   Allow ~30 minutes to reach temperature and stabilize.
   Temperature in flask will be offset from setting on plate by ~17 °C lower.
   (i.e. set: 225 °C → flask: ~208 °C)

6. Put stir bar into reaction flask. Put thermocouple into the flask at this point if necessary, sealing it between the glass and the septum. 7. Put septum onto flask to seal it. 8. Clamp reaction flask in 3-finger clamp. 9. Lower the reaction flask into the oil bath. Make sure the flask is not touching the bottom of the dish.	
10. Press stirrer button on plate. Set to desired stir speed. 11. When finished with reaction, turn off heater and stirrer. 12. Raise clamped flask out of oil bath and clean oil off with kimwipe with toluene and then acetone. 13. Allow oil bath to come to room temperature.	

Se-TOP Procedure

1. Purge Octadecene (ODE) following the ***Purging Procedure*** for ~15 minutes.
2. Weigh out 33 mg Se powder into a 50 mL round bottom flash. Make sure the flask is clean and dry.
3. Drop a small stir bar in the flask. Cap flask with a rubber septum.



*Do **NOT** breathe in Selenium fumes.*

4. Clamp the neck of the flask in a 3-finger clamp on ring stand.
5. Set heat to 150 °C.
6. Purge the flask with N_2 gas by inserting the purge needle followed by a venting needle. Allow to purge for 10 minutes.

7. Transfer 5 mL ODE into the flask using the ***Syringing Procedure.***

8. Lower flask into oil bath.

9. Set stir to 500 rpm.

10. Begin purging trioctylphosphine using the ***Purging Procedure***.
    Purge for ~15 minutes.

11. Using the ***Syringing Procedure***, add 0.4 mL of purged TOP to the Se-TOP reaction flask. The majority of the selenium should dissolve immediately.

12. Continue stirring at 150 °C until the solution is completely clear. If all the selenium does not dissolve, it may be a sign that oxygen was introduced into the reaction and oxidize the TOP before the selenium and TOP can react.

13. Remove the solution from the oil bath and pull out the N_2 needle and vent needle.

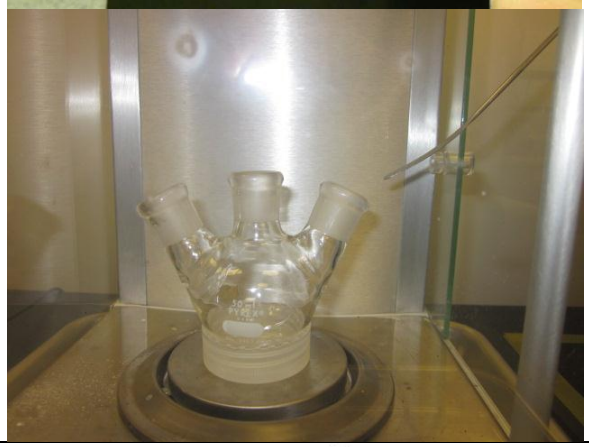
14. Once it has cooled, clean the outside of the flask with toluene and acetone.

    This SeTOP solution can be stored for up to a week and makes enough SeTOP precursor for five QD syntheses.

Cd-Precursor Procedure

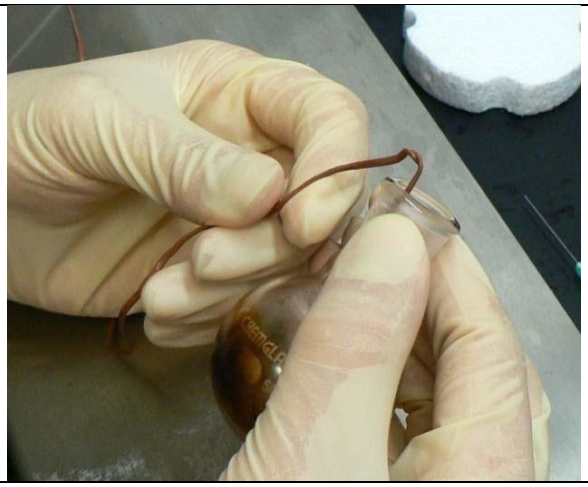
1. Weigh out 13 mg of CdO into a 50 mL round bottom flask.

2. Put a small stir bar into the bottom of the flask.




*Cadmium Oxide is Toxic. Do **NOT** breathe fumes.*


3. Insert a thermocouple so that the wire almost touches the bottom of the flask.



4. Place a rubber septum onto the flask and fold over the edges to firmly secure the thermocouple.	

5. Clamp the flask in a 3-finger clamp on a ring stand and begin purging with N_2 using the ***Purging Procedure***. Purge for ~10 minutes.

6. Set heat on oil bath to 242 °C (Adjust as needed to achieve 225 °C in flask).

7. Using the ***Syringing Procedure***, add 10 mL of purged ODE into the flask.
8. Lower the flask into the oil bath.
9. Set the stir function to 500 rpm.

10. Purge the Oleic Acid using the ***Purging Procedure*** for ~10 minutes.

11. Using the ***Syringing Procedure***, add 0.6 mL Oleic Acid to the Cd reaction flask.

12. Heat until solution becomes optically clear. CdO has a tendency to stick to the walls of the flask, so the flask should be agitated occasionally to prevent build up on walls.

*Some chemicals in this reaction mixture become volatile around 200 °C. Do **NOT** breathe fumes.*

Sample Removal

Caution: *This process requires safely handling high-temperature organic, volatile chemicals. Two people must be present and all those present must wear appropriate safety equipment at all times.*

Prepare syringes and vials while the Cd precursor is heating.

1. Attach one metal needle tip securely to a plastic 3 mL syringe and one to a glass 5 mL syringe with Luer lock.

2. Remove the caps from clean, dry vials.

3. Once the Cd precursor becomes optically clear, ensure that its temperature is stable at 225 °C (adjust hot plate setting as needed to achieve stability at 225 °C).

4. Once stable at 225 C, **quickly** inject 1 mL of room-temperature Se-TOP precursor into the hot Cd precursor.

   Start timing when the SeTOP precursor is injected.

   A white fog will immediately form and the solution will begin changing color to a pale yellow.

5. Using the glass syringe, **carefully** remove samples of 0.5 to 3 mL at desired time intervals. 6. Put samples into separate vials.	
7. Cap and label the vials, indicating quantum dot type, date synthesized, reaction time, and absorbance wavelength.	

Appendix B

	Ratio 1		Ratio 2		Ratio 3		Ratio 4	
Red (mL)	0.25		0.25		0.5		0.75	
Green (mL)	1.75		1.25		1		0.5	
Octadecene (mL)	0		0.75		0.5		0.75	
Yellow (mL)	0		0		0		0	
CIE Values (x,y)	*0.296*	*0.496*	*0.375*	*0.569*	*0.371*	*0.464*	*0.412*	*0.433*

	Ratio 5		Ratio 6		Ratio 7		Ratio 8	
Red (mL)	0.875		0.5		0.75		0.5	
Green (mL)	0.25		0.25		0.25		0.25	
Octadecene (mL)	0.875		1		1		1.25	
Yellow (mL)	0		0		0		0	
CIE Values (x,y)	*0.476*	*0.418*	*0.423*	*0.435*	*0.444*	*0.421*	*0.411*	*0.417*

	Ratio 9		Ratio 10		Ratio 11		Ratio 12	
Red	0.25		0.25		0.25		0.3	
Green	0.25		0.2		0.2		0.15	
Octadecene	1.5		1.55		1.55		1.4	
Yellow	0		0		0.25		0.1	
CIE Values	*0.342*	*0.427*	*0.356*	*0.422*	*0.348*	*0.491*	*0.358*	*0.463*

	Ratio 13		Ratio 14		Ratio 15		Ratio 16	
Red (mL)	0.3		0.4		0.4		0.3	
Green (mL)	0.15		0.15		0.15		0.15	
Octadecene (mL)	1.55		1.45		1.45		1.55	
Yellow (mL)	0		0		0		0	
CIE Values (x,y)	*0.386*	*0.405*	*0.417*	*0.409*	*0.487*	*0.388*	*0.467*	*0.389*
					(ZnS Coated)		(ZnS Coated)	

Appendix C

QUANTUM DOT LAB INVENTORY	

Chemicals					
Name	*Supplier/Manuf*	*Quality/Condition*	*Item #*	*Amount per Synthesis*	*Unit Price*
Octadecene	Sigma Aldrich	90% Tech Grade	O806-1L	~30 ml	$24.10
Oleic Acid	Sigma Aldrich	90% Tech Grade	364525-1L	0.6 ml	$41.80
CdO Powder	Alfa Aesar	98.9%	33325	14 mg	$30.90
Se Powder	Sigma Aldrich	99%	209651-50g	33 mg	$35.10
Trioctylphosphine	Sigma Aldrich	90% Tech Grade	117854-25ml	1 mL	$34.60

Consumables					
Name	*Supplier/Manuf*	*Quality/Condition*	*Item #*	*Amount Per Synthesis*	*Unit Price*
Nitrile Gloves	Valutek	Large, 9.5"	VTGNPFX95	2 to 4	$114.33
Needles 20G11/2	FisherSci/BD Biosciences	20 gauge 1.5 inch	BD 305176/ Fisher	3	$5.36
3 ml syringes	Sigma Aldrich		Z116858	1	$25.20
1 ml syringes	Sigma Aldrich		Z230723	1	$50.80
Septa	Sigma Aldrich	Suba-Seal	Z124591	1	$97.20